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Biomass Waste, Coffee Grounds-derived Carbon for Lithium Storage

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ABSTRACT

Biomass waste-derived carbon is an attractive alternative with environmental benignity to obtain carbon material. In this study, we prepare carbon from coffee grounds as a biomass precursor using a simple, inexpensive, and environmentally friendly method through physical activation using only steam. The coffee-derived carbon, having a micropore-rich structure and a low extent of graphitization of disordered carbon, is developed and directly applied to lithium-ion battery anode material. Compared with the introduction of the Ketjenblack (KB) conducting agent (i.e., coffee-derived carbon with KB), the coffee-derived carbon itself achieves a reversible capacity of ~200 mAh/g (0.54 lithium per 6 carbons) at a current density of 100 mA/g after 100 cycles, along with excellent cycle stability. The origin of highly reversible lithium storage is attributed to the consistent diffusion-controlled intercalation/de-intercalation reaction in cycle life, which suggests that the bulk diffusion of lithium is favorable in the coffee-derived carbon itself, in the absence of a conducting agent. This study presents the preparation of carbon material through physical activation without the use of chemical activation agents and demonstrates an application of coffee-derived carbon in energy storage devices.

Keywords : Biomass, Coffee, Disordered carbon, Micropore, Lithium-ion batteries

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1. Introduction

Carbons have become more attractive materials with highly diverse properties and applications. Their highly adsorptive ability is applied in many adsorption and catalytic processes [1-3]. In lithium-ion batteries (LIBs), carbons have been studied for decades, and graphite is used as an anode material in commercial LIBs with a theoretical capacity of 372 mAh/g (LiC_6, one lithium per six carbons) and has excellent cycle stability during cycling [4,5]. However, the disadvantage of graphite is that it is relatively expensive to prepare and has a rather low lithium storage per carbon weight (LiC_6) [6]. To explore the alternatives to graphitic carbons for LIB anodes, significant effort is being committed [6,7], and soft carbons and hard carbons are obtained in several ways. More recently, carbon has been developed from various biomasses, and the naturally-derived carbon precursors are regarded as an attractive choice, in that the biomass-derived carbon provides an alternative method in waste and by-product management and has an intrinsically desirable molecular structure for charge stor-

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age and transport [8,9]. In particular, the biomass-derived carbons from industrial or domestic waste, such as waste paper [10,11], sugar cane bagasse [12,13], rubber wood sawdust [14], and used tea dust waste [15] are designed to realize the concept of sustainable carbon.

Approximately eight million metric tons of coffee is produced globally each year, and most is discarded as a waste by beverage manufactures in the form of coffee grounds [16]. Coffee grounds are composed of mostly cellulose-based materials [17,18]. The fibrous structure (e.g., hemicellulose and cellulose) has a less robust and a more labile nature compared to lignin, so that the activation process of carbonaceous materials with a rich fibrous structure is easier than for materials having a higher proportion of lignin [19,20]. Indeed, the carbon obtained through the activation of cellulose in coffee is explored as electrode materials for LIBs [21] and supercapacitors [22-24]. A traditional activation process for carbonization is accomplished by a chemical reagent of potassium hydroxide (KOH), followed by a heat- treatment at high-temperatures [25,26]. KOH is known to facilitate dehydration and decomposition reactions at the initial stage of activation, and consequently has a beneficial effect on the formation of micropores. However, the environmental hazards and chemical toxicity of KOH, along with the complex multistep activation processes, hinder the development of low-cost activation of carbon with environmental benignity [25-27].

Herein, we prepare the carbon derived from coffee grounds as a biomass precursor by using a simple, inexpensive, and environmental friendly method through physical activation using only steam. Micropore-rich carbon is obtained in the coffee-derived carbon, along with a low extent of graphitization of disordered carbon, and the coffee-derived carbon is directly applied to an anode material for LIBs. This study explores the potential of coffee for utilization in lithium transport and storage, and also demonstrates the reversible lithium storage of coffee-derived carbon in energy storage devices.

2. Experimental

The coffee grounds, after leaching with cold water at room temperature, were prepared as a starting material for obtaining a carbon. The coffee grounds were carbonized under continuous N_2 gas at 200 cm^3 STP/min. The 600°C carbonization temperature was reached at a 10°C/min heating rate and was maintained for 2 h. For the activation process, 300 cm^3 STP/min of N_2 gas was continuously fed into the reactor and, at the same time, only steam was used as an activation agent. Under a 2 mL-H_2O/g-char h steam flow rate, the activation process was conducted at 800°C for 2 h. After activation, to prevent oxidation, the sample was cooled inside a furnace under N_2 gas flow, and the obtained carbon is referred to as coffee-derived carbon in this work.

For electrochemical measurements, a working electrode was fabricated by mixing the coffee-derived carbon powder as an active material, and polyvinylidene difuluoride (PVDF) as a binder at a weight ratio of 70:30 in an N-methyl-2-pyrrolidone solvent. For comparison, an electrode including the KB conductive agent was also designed as control group at a weight ratio of 70:15:15. The mixed slurry was plastered onto a copper foil current collector with a doctor blade and dried under a vacuum at 120°C for 8 h. The dried slurry was punched to a size of 11 mm in diameter to fit the electrode size. A 2032-type coin cell, consisting of the working electrode and lithium metal both as a counter and as reference electrodes was assembled in a glove box under a dry argon atmosphere. The organic electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a volume ratio of 1:1. Galvanostatic discharge/charge measurements (WBCS3000, Wonatech) were carried out on the coin cell in the voltage range 0.01-3 V (*vs.* Li^+/Li) at a current density of 100 mA/g.

3. Results and Discussion

Just after activation, the coffee-derived carbon is obtained in the form of a powder, as shown in Fig. 1a. In Fig. 1b, FE-SEM images of the particles (several hundred micrometers in size) are shown. At a higher magnification (Fig. 1c), one particle consists of a bundle of pores having a diameter of several tens of micrometers. In addition, as shown in Fig. 1d, the pores are divided into two categories, clogged pores (one of which is indicated by the white arrow) and open pores (one of which is indicated by the green arrow). During the activation process, the steam going through the interior of a particle enables the

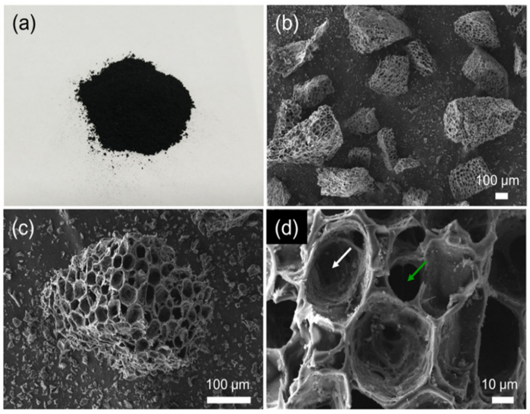

Fig. 1. (a) Photograph, and (b-d) FE-SEM images of the coffee-derived carbon after the activation process.

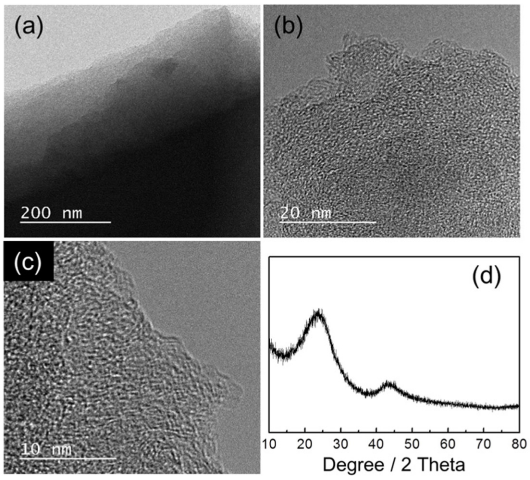

Fig. 2. (a-c) HR-TEM images, and (d) XRD pattern of the coffee-derived carbon.

coffee-derived carbon to have open pores with a hollow structure.

The morphology of coffee-derived carbon was further investigated by using HR-TEM images in Fig. 2a-c. To prepare the specimen for TEM analysis, the carbon particle was ground by hand in a mortar owing to its weak hardness, and its fragments are shown in Fig. 2a. Moreover, in the higher magnification images (Fig. 2b and c), small graphitic sheets having random orientation are observed; therefore, the disordered carbon structure is confirmed in the coffee-derived carbon [28,29]. To identify the chemical composition of coffee-derived carbon quantitatively, TEM/EDS analyses were conducted. Approximately 84 wt% of carbon and 10 wt% of oxygen were confirmed in Table 1, along with small quantities of magnesium, phosphorous, potassium and calcium, in which the inorganic species are generally observed in woody biomasses [30,31]. The crystalline structure of coffee-derived carbon was examined through X-ray diffraction (XRD) analysis in Fig. 2d. Two peaks of approximately 23° and 43° are, respectively, ascribed to (002) and (100) reflections from the typical graphite, and the considerable broadness of the peaks implies that the coffee-derived carbon has the defective structure of disordered carbon [29].

Table 1. EDS results for coffee-derived carbon.

Element	Weight %	Atomic %
C	83.70	89.65
O	10.09	8.11
Mg	0.83	0.44
P	0.62	0.25
K	3.71	1.22
Ca	1.04	0.33

From nitrogen adsorption/desorption isotherm and pore size distribution, the surface area and porosity of the coffee-derived carbon were examined. The isotherm in Fig. 3a corresponds with type I of the IUPAC classification [32], which indicates a dominant contribution of micropores inside a material with relatively small external surfaces, such as activated carbon and molecular sieve zeolite [32]. The surface area obtained is 503 m^2 g^{-1}, and the dominant size of the micropores is approximately 2.5 nm as shown in Fig. 3b.

To evaluate the lithium storage properties of coffee-derived carbon as an anode material for LIBs, electrochemical measurements were conducted in the range of 0.01-3 V at a constant current density of 100 mA/g, as shown in Fig. 4. As described in section 2, for examining the inherent performance of coffee-derived carbon toward lithium storage, the electrode of coffee-derived carbon is composed only of coffee-derived carbon and a binder, in the absence a conduction agent. However, for comparison, the electrode including the KB conduction agent was also designed as a control group, referred to as coffee-derived carbon with KB. Fig. 4a shows the cycle

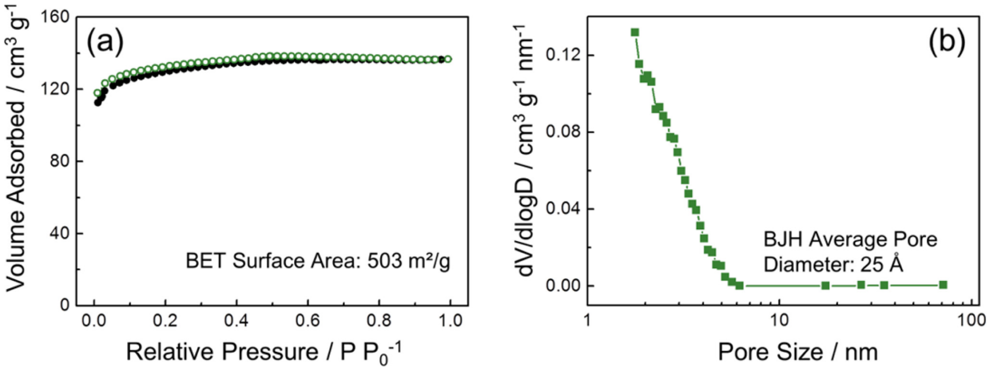

Fig. 3. (a) Nitrogen adsorption/desorption isotherm, and (b) pore size distribution of coffee-derived carbon.

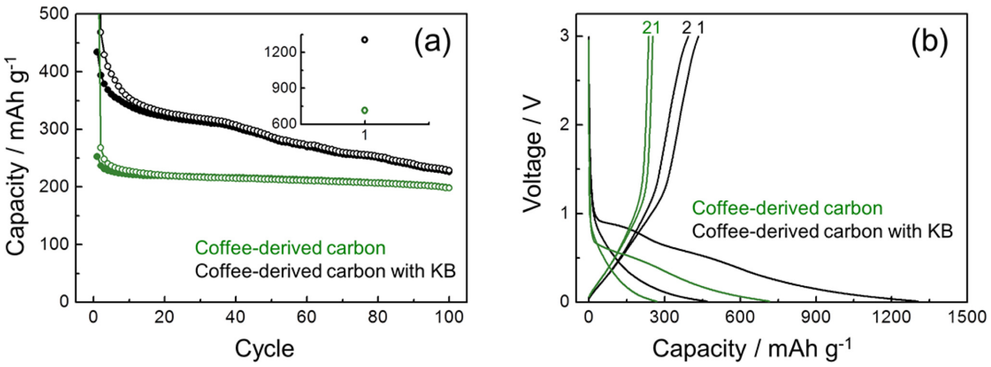

Fig. 4. (a) Cycle performance, and (b) voltage profile of coffee-derived carbon and coffee-derived carbon with KB electrodes.

performance of both electrodes. Although a higher capacity of coffee-derived carbon with KB is observed during 100 cycles compared with coffee-derived carbon, in which the 100th charge capacity of coffee-derived carbon with KB and coffee-derived carbon is observed as ~230 mAh/g and ~200 mAh/g, respectively, the coffee-derived carbon electrode has considerably more stable capacity retention. The 100th capacity of 200 mAh/g with stable capacity retention implies that the coffee-derived carbon delivers 0.54 lithium per 6 carbons reversibly. Although the capacity ~200 mAh/g is lower than the theoretical capacity of graphite (372 mAh/g), its stable cyclability demonstrates the reversible lithium insertion/desertion into/from the coffee-derived carbon. In the first two voltage profiles of coffee-derived carbon with KB and coffee-derived carbon (Fig. 4b), no obvious plateau is observed under 0.4 V during the discharge process, which infers a characteristic of lithium storage in disordered carbon having a low extent of graphitization [33]. Moreover, during the charge process, the slope inflection with a fiducial point ~1 V suggests that the de-lithiation can be separated into two reaction processes based on the 1 V as follows: under 1 V, de-intercalation from the carbon interlayer by lithium diffusion; and over 1 V, desorption at the carbon surface by electrochemical double-layer capacitor (EDLC)-like capacitive behavior [33,34].

To understand the manner of lithium storage in detail, along with the capacity origin of high lithium storage in coffee-derived carbon with KB, the differential capacity profiles (dQ/dV *vs*. voltage) of coffee-derived carbon and coffee-derived carbon with KB at the selected cycles are compared in Fig. 5. The wider area under 1 V than that over 1 V during all the differential capacity profiles indicates the dominant lithium storage by diffusion, corresponding to the higher

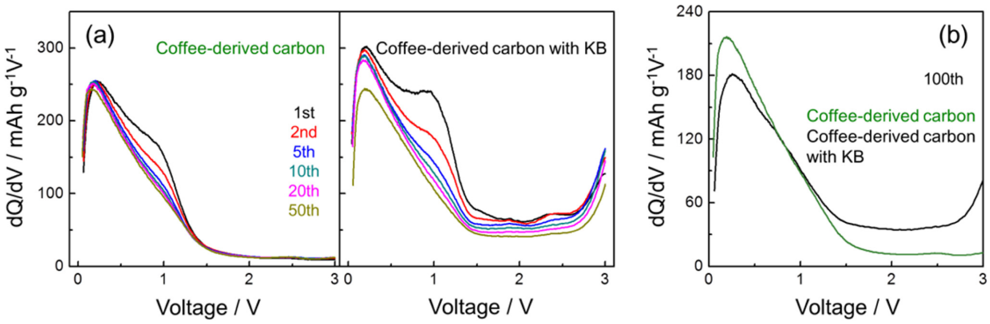

Fig. 5. (a) Differential capacity profiles upon the de-lithiation process, and (b) comparison of 100th differential capacity profiles of the coffee-derived carbon and the coffee-derived carbon with KB electrodes.

bulk contribution than surface contribution, in both electrodes (Fig. 5a). It is also confirmed that the robust bulk utilization of coffee-derived carbon compared with coffee-derived carbon with KB, implies that the inherent structure of coffee-derived carbon is favorable for the lithium intercalation/de-intercalation into/from the carbon interlayer. In Fig. 5a, the higher capacity of coffee-derived carbon with KB compared with coffee-derived carbon is originated from both the bulk and surface reaction processes during 50 cycles. More importantly, the reverse contribution of bulk and capacitive storage is confirmed between coffee-derived carbon and coffee-derived carbon with KB after 100 cycles as shown in Fig. 5b. This observation suggests that the lithium storage with diffusion-controlled de-intercalation is favorable in the coffee-derived carbon itself, without the introduction of the KB conducting agent.

4. Conclusions

Carbon derived from coffee grounds, which is a biomass waste, was synthesized by a simple, inexpensive, and environmentally friendly method through physical activation using only steam. Micropore-rich carbon with a low extent of graphitization of disordered carbon structure was developed from coffee-derived carbon and directly applied to an anode material for LIBs. The coffee-derived carbon itself achieved a reversible capacity of ~200 mAh/g at a current density of 100 mA/g after 100 cycles, along with excellent cycle stability. Compared with coffee-derived carbon with KB, the highly reversible lithium storage of coffee-derived carbon originates from the consistent diffusion-controlled intercalation/de-intercalation reaction in cycle life, suggesting that the inherent structure of coffee-derived carbon is favorable for lithium storage. This study explored the potential of coffee for utilization in lithium transport and storage, and demonstrated that coffee-derived carbon is a promising material source with environmental benignity for energy storage electrodes.

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